Theory of Collision-Broadened Ion Cyclotron Resonance Spectra

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A formalism for calculating collision-broadened ion cyclotron resonance spectra is developed in detail. The Boltzmann transport equation describing the time variation of the arbitrary function of ion velocity $X(\mathbf{v})$ is extended to include resonant charge transfer. Then with $X(\mathbf{v})=\mathbf{v}$ and $X(\mathbf{v})=v^2$, equations describing, respectively, the velocity and energy of an average particle are developed. The solution of these equations is used to obtain the power absorption of the ions from the observing radio-frequency electric field.

The effects of collisions are treated in terms of specific ion–molecule interactions. The equations of motion for a mixture of ions, A and B, are coupled by the collision term which accounts for the charge-transfer process $A^+ + B \rightleftarrows A + B^+$. As numerical examples the collision frequencies are evaluated for the rare gases and used to calculate absorption spectra for Ar^+ in Ar and mixtures of He and Ne isotopes. The formalism permits the straightforward examination of the effects of electric-field strength, pressure, and temperature on the line shapes.

I. INTRODUCTION

A CHARGED particle moving in a uniform magnetic field **H** describes a circular orbit in a plane perpendicular to **H**. The angular frequency or cyclotron frequency ω_c of this motion is independent of the velocity of the ion and is given by

$$\omega_c = qH/mc, \tag{1}$$

where q is the charge of the particle, H is the magnetic field strength, m the particle mass, and c the speed of light.[1] When an alternating electric field $\mathbf{E}(t)$ is applied normal to **H** at the cyclotron frequency, the ions can absorb energy from the alternating field and are accelerated to larger velocities with increased orbital radii.

Cyclotron resonance is observed in both gases and solids. In solids the absorption by free electrons and holes occurs at a frequency given by Eq. (1) with the substitution of an effective mass m^* for the electron mass.[2] In solids the particles undergoing cyclotron resonance are generally subject to forces which extend over the entire orbit of the particles. Cyclotron resonance can be observed in highly ionized gases (plasmas), the effect being complicated by the collective phenomena resulting from the long-range Coulombic interactions.

In gases where charged particle densities are such that Coulombic interactions can be neglected, the particles are subject to a stochastic rather than a continuous force. This force arises from the effects of collisions that are limited both in time and space with respect to the over-all motion of the charged particles. Under such conditions it is possible to write a phenomenological equation of motion for the velocity of the particle with a damping term representing the effects of collisions. Such an equation of motion has been used[3] to describe ion cyclotron resonance.

Electron cyclotron resonance has received more attention from a theoretical standpoint. In the limit that the charged particle mass is small compared to the mass of the scattering particle it is possible to obtain an approximate solution to the Boltzmann equation[4–6] which can be employed to calculate electron cyclotron resonance line shapes.[4,7]

The line shapes obtained in cyclotron resonance experiments yield information about the collision processes responsible for the damping of the charged particle motion. Wobschall, Graham, and Malone have derived collision cross sections for several ions from the linewidths of ion cyclotron resonance spectra.[3] Cross sections for the interactions of electrons with gases have been analyzed by electron cyclotron resonance in rf discharges[8] and afterglows.[7]

In this paper the theory of collision-broadened ion cyclotron resonance line shapes is examined in detail. In Appendix I and Sec. II the Boltzmann transport equation for a molecular property is extended to include the effects of resonant charge transfer. From this a phenomenological equation of motion for the ions is developed which permits the effects of collisions to be treated in a straightforward manner. The effects of collisions are examined for a number of cases, including (1) elastic collisions of ions with neutral molecules where charge transfer is not important and

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(2) collisions of ions in their parent gases for a single isotope (Case I) where charge transfer can be an important process, and collisions of ions with neutral species for a mixture of isotopes (Case II), where charge transfer leads to coupling between the equations of motion of the different ion components. The phenomenological equation developed in Sec. II is solved and used to calculate the rf power absorption in Sec. III. The results describe the variation of the line shape with temperature, pressure, and electric field, the external parameters which can be varied in an experiment. In Sec. IV the collision frequencies are evaluated from the parameters describing ion–molecule interactions. These are the internal parameters which are to be determined in an experiment. Specific examples of the application of the theory are developed in Sec. V.

II. DERIVATION OF THE PHENOMENOLOGICAL EQUATION OF MOTION

A. Boltzmann Transport Equation for Molecular Properties

The Boltzmann equation as it applies to transport properties of ionized gases is developed extensively by Chapman and Cowling.[6] Allis has also treated ionized gases in electromagnetic fields using the Boltzmann equation.[5] It is assumed that the velocities of the ions can be described by a distribution function $f(\mathbf{v}_i)$ such that there are $f(\mathbf{v}_i)d\mathbf{v}_i$ ions within the volume element $d\mathbf{v}_i$ centered at $\mathbf{v}_i$ in velocity space. $f(\mathbf{v}_i)$ is normalized to n_i^+, the ion number density. It is further assumed that the ion cyclotron resonance experiment is conducted in such a fashion as to exclude any spatial variation of the distribution function. The Boltzmann equation can be solved by an expansion of the distribution function in spherical harmonics about the direction of $\mathbf{E}(t)$ in the case of electrons.[4] With ions in gases where the ion mass is comparable to the mass of the neutral species the convergence of the expansion is poor. The usual recourse is to employ the transport equation for molecular properties which is derived from the Boltzmann equation and is given by Allis[9] excluding the space gradient term as

$$(\partial/\partial t)[n_i^+\langle X(\mathbf{v}_i)\rangle_{\mathrm{Av}}] = \frac{q_i n_i^+}{m_i}\left\langle\left[\mathbf{E}(t)+\frac{\mathbf{v}_i\times\mathbf{H}}{c}\right]\cdot\frac{\partial X(\mathbf{v}_i)}{\partial \mathbf{v}_i}\right\rangle_{\mathrm{Av}} + \sum_j\int[X(\mathbf{v}_i')-X(\mathbf{v}_i)]f(\mathbf{v}_i)F(\mathbf{V}_j)v_{ij}bdbd\epsilon d\mathbf{v}_i d\mathbf{V}_j, \quad (2)$$

where $\mathbf{v}_i$ is the velocity of ion species i, $\mathbf{V}_j$ is the velocity of neutral species j, $X(\mathbf{v}_i)$ is an arbitrary function of the ion velocity, v_{ij} is the relative velocity given by $|\mathbf{v}_i-\mathbf{V}_j|$, and $F(\mathbf{V}_j)$ is the Maxwellian distribution function for neutrals given by

$$F(\mathbf{V}_j)=n_j(m_j/2\pi kT)^{3/2}\exp(-m_jV_j^2/2kT). \quad (3)$$

The scattering parameters in Eq. (2) are b, the initial impact parameter; ϵ, the scattering azimuth; and θ, the angle through which the relative velocity vector $\mathbf{v}_{ij}$ is turned on collision. The particles interact and are scattered elastically from $\mathbf{v}_i$ and $\mathbf{V}_j$ to $\mathbf{v}_i'$ and $\mathbf{V}_j'$ in velocity space. $X(\mathbf{v}_i')$ in Eq. (2) is in general a function of θ, ϵ, b, and v_{ij}. The averages indicated in Eq. (2) are over the ion velocity distribution function. The first term on the right side of Eq. (2) represents the rate of change of $X(\mathbf{v}_i)$ due to the external fields. The second term represents the rate of change of $X(\mathbf{v}_i)$ due to collisions.

Resonant charge transfer is an important process for ions in their parent gases. Charge-transfer effects are not easily included in Eq (2) as it is written. Let $X_c(\mathbf{v}_i')$ represent the value which $X(\mathbf{v}_i)$ takes following a collision in which charge transfer occurs. Let P_{ij} be the probability of charge transfer on collision between ions i with neutrals j. If there are N ion components in the system under consideration then there are $3N-1$ collision events which must be accounted for in the extension of Eq. (2). For each ion interacting with its parent neutral there are two processes represented by

$$i^+ + i \rightarrow i^+ + i, \quad (4a)$$

$$i^+ + i \rightarrow i + i^+. \quad (4b)$$

For each other ion j and its corresponding parent neutral there are three interactions which affect ion component i. These are

$$i^+ + j \rightarrow i^+ + j, \quad (4c)$$

$$i^+ + j \rightarrow i + j^+, \quad (4d)$$

$$i + j^+ \rightarrow i^+ + j. \quad (4e)$$

Equation (2) is extended to include the effects of charge transfer in Appendix I. Using the results of Appendix I to account for Processes (4a)–(4e) gives

$$\begin{aligned}(\partial/\partial t)[n_i^+\langle X(\mathbf{v}_i)\rangle_{\mathrm{Av}}] &= \frac{q_i n_i^+}{m_i}\left\langle\left[\mathbf{E}(t)+\frac{\mathbf{v}_i\times\mathbf{H}}{c}\right]\cdot\frac{\partial X(\mathbf{v}_i)}{\partial \mathbf{v}_i}\right\rangle_{\mathrm{Av}} \\ &+\int[X(\mathbf{v}_i')-X(\mathbf{v}_i)](1-P_{ii})\lambda_{ii}d\tau_{ii} \\ &+\int[X_c(\mathbf{v}_i')-X(\mathbf{v}_i)]P_{ii}\lambda_{ii}d\tau_{ii} \\ &+\sum_{j\neq i}\int[X(\mathbf{v}_i')-X(\mathbf{v}_i)](1-P_{ij})\lambda_{ij}d\tau_{ij} \\ &-\sum_{j\neq i}\int X(\mathbf{v}_i)P_{ij}\lambda_{ij}d\tau_{ij}+\sum_{j\neq i}\int X_c(\mathbf{v}_i')P_{ji}\lambda_{ji}d\tau_{ji}, \quad (5)\end{aligned}$$

[9] Reference 5, Eq. (37.3).

where

$$\lambda_{ij}=f(\mathbf{v}_i)F(\mathbf{V}_j)$$

and

$$d\tau_{ij}=v_{ij}bdbd\epsilon d\mathbf{v}_i d\mathbf{V}_j.$$

The five collision terms in Eq. (5) represent, respectively, Processes (4a)–(4e). To develop a phenomenological equation of motion from (5) requires a consideration of the collision in velocity space.

B. Collision in Velocity Space

Let $\mathbf{V}_c$ and $\mathbf{v}_{ij}$ be, respectively, the center-of-mass velocity and relative velocities of particles i and j:

$$\mathbf{V}_c=(m_i\mathbf{v}_i+m_j\mathbf{V}_j)/(m_i+m_j), \tag{6}$$

$$\mathbf{v}_{ij}=\mathbf{v}_i-\mathbf{V}_j. \tag{7}$$

In an elastic collision both $\mathbf{V}_c$ and v_{ij} remain unchanged to conserve momentum and energy. $\mathbf{v}_{ij}$ changes in direction, being turned through an angle θ to $\mathbf{v}'_{ij}$. This is shown in Fig. 1. Because of the conservation relations $\mathbf{v}_i$ is scattered onto a sphere of radius $m_j v_{ij}/(m_i+m_j)$ centered at $\mathbf{V}_c$. Similarly $\mathbf{V}_j$ is scattered onto a sphere of radius $m_i v_{ij}/(m_i+m_j)$ centered also at $\mathbf{V}_c$. If an ion of species i collides with a Neutral i and charge transfer occurs, then the ion appears to have been scattered through an angle $\pi-\theta$, θ remaining as labeled in Fig. 1.

C. Phenomenological Equation of Motion

To obtain an equation of motion for an average particle, let $X(\mathbf{v}_i)=\mathbf{v}_i$. Assume steady-state conditions with regard to n_i^+ such that $\partial n_i^+/\partial t=0$. Equation (5) then reduces to

$$\frac{\partial\bar{\mathbf{v}}_i}{\partial t}=\frac{q_i\mathbf{E}(t)}{m_i}+\frac{q_i\bar{\mathbf{v}}_i\times\mathbf{H}}{m_i c}+\left(\frac{\partial\mathbf{v}_i}{\partial t}\right)_{\text{coll}}, \tag{8}$$

where the bar indicates the average over the ion velocity distribution and the last term on the right represents the effect of collisions.

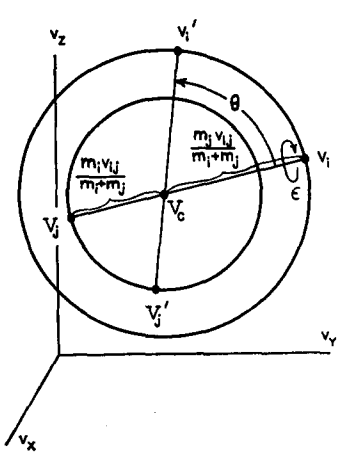

FIG. 1. Effects of an elastic collision in velocity space. $\mathbf{V}_c$ and v_{ij} are not changed by the collision. If charge transfer occurs then $\mathbf{v}_i'$ and $\mathbf{V}_j'$ become $\mathbf{V}_i'$ and $\mathbf{v}_j'$ respectively, with θ remaining as labeled.

1. Elastic Collisions

With $P_{ij}=0$ (no charge transfer) the collision term becomes

$$(\partial\mathbf{v}_i/\partial t)_{\text{coll}}=(n_i^+)^{-1}\sum_j\int(\mathbf{v}_i'-\mathbf{v}_i)\lambda_{ij}d\tau_{ij}, \tag{9}$$

where the summation is over all neutral components of the gas. Expressing $\mathbf{v}_i'$ in terms of $\mathbf{v}_i$, $\mathbf{V}_j$, and the scattering parameters it is found on integrating over the azimuth that

$$\int_0^{2\pi}(\mathbf{v}_i'-\mathbf{v}_i)d\epsilon=-\frac{2\pi m_j}{m_i+m_j}(1-\cos\theta)(\mathbf{v}_i-\mathbf{V}_j). \tag{10}$$

The terms on the right of Eq. (10) involving $\mathbf{V}_j$ will vanish in Eq. (9) on integration over $d\mathbf{V}_j$. Define ν_{ij}^e as an elastic collision frequency between ions i and neutrals j by

$$\nu_{ij}^e=\frac{v_{ij}n_j m_j}{m_i+m_j}2\pi\int_0^\infty(1-\cos\theta)bdb$$
$$=[v_{ij}n_j m_j/(m_i+m_j)]q_d, \tag{11}$$

where q_d is the diffusion cross section of kinetic theory. The collision term now becomes

$$(\partial\mathbf{v}_i/\partial t)_{\text{coll}}=-\sum_j(n_j n_i^+)^{-1}$$
$$\times\int\nu_{ij}^e\mathbf{v}_i f(\mathbf{v}_i)F(\mathbf{V}_j)d\mathbf{v}_i d\mathbf{V}_j. \tag{12}$$

An evaluation of the right side of Eq. (12) requires an analysis of ν_{ij}^e to determine its velocity dependence. This is done in Sec. IV. The velocity averaging in Eq. (12) requires a knowledge of $f(\mathbf{v}_i)$. Since this is not available, it is necessary to make an assumption which permits an approximate evaluation of Eq. (12). Equation (12) is factored to give

$$\left(\frac{\partial\mathbf{v}_i}{\partial t}\right)_{\text{coll}}=-\sum_j\left(\frac{1}{n_j n_i^+}\int\nu_{ij}^e f(\mathbf{v}_i)F(\mathbf{V}_j)d\mathbf{v}_i d\mathbf{V}_j\right)$$
$$\times\left(\frac{1}{n_i^+}\int\mathbf{v}_i f(\mathbf{v}_i)d\mathbf{v}_i\right)$$
$$=-\sum_j\xi_{ij}^e\bar{v}_i, \tag{13}$$

where ξ_{ij}^e is the velocity average of ν_{ij}^e. The assumption inherent in writing Eq. (13) is that the average of the product $\nu_{ij}^e\mathbf{v}_i$ can be approximated by the product of the averages. This amounts to assuming that ν_{ij}^e and $\mathbf{v}_i$ are independent, which is true only in the case that ν_{ij}^e is independent of v_{ij}. If ν_{ij}^e is not a strong function of velocity then the error in Eq. (13) will be minimal. It is shown in Sec. IV that this is usually the case.

Equation (8) can now be written

$$\frac{\partial\bar{\mathbf{v}}_i}{\partial t}=\frac{q_i\mathbf{E}(t)}{m_i}+\frac{q_i\bar{\mathbf{v}}_i\times\mathbf{H}}{m_i c}-\sum_j\xi_{ij}^e\bar{\mathbf{v}}_i, \tag{14}$$

which is identical to the phenomenological equation of motion for an average particle employed by Wobschall and his co-workers.[3]

The effects of charge transfer are now to be included. There are two cases to be considered. The first treats a single isotope moving in its parent gas; the second a mixture of isotopes.

Case I (single isotope): The collision term in Eq. (8) now becomes

$$(\partial \mathbf{v}_i/\partial t)_{\text{coll}} = (n_i^+)^{-1}\int (\mathbf{v}_i' - \mathbf{v}_i)(1-P_{ii})\lambda_{ii} d\tau_{ii}$$

$$+(n_i^+)^{-1}\int [(\mathbf{v}_i')_c - \mathbf{v}_i] P_{ii}\lambda_{ii} d\tau_{ii}, \quad (15)$$

where the subscript c refers to $\mathbf{v}_i'$ following charge transfer. Using the fact that if charge transfer occurs the particle appears to be scattered through an angle $\pi-\theta$ gives

$$\int [(\mathbf{v}_i')_c - \mathbf{v}_i] d\epsilon = -\pi(1+\cos\theta)(\mathbf{v}_i - \mathbf{V}_i). \quad (16)$$

Then we define a charge-transfer collision frequency (the reason for this terminology is made evident in Sec. IV) by

$$\nu_{ii}^c = n_i v_{ii}\pi\left[\int_0^\infty (1-P_{ii})(1-\cos\theta) b db + \int_0^\infty (1+\cos\theta) P_{ii} b db\right]$$

$$= n_i v_{ii}\pi\left[\int_0^\infty (1-\cos\theta) b db + 2\int_0^\infty P_{ii}\cos\theta b db\right]. \quad (17)$$

Making the same factorization as in Eq. (13) and defining ξ_{ii}^c in the same manner as ξ_{ii}^e permits the collision term to be written as

$$(\partial \mathbf{v}_i/\partial t)_{\text{coll}} = -\xi_{ii}^c \bar{\mathbf{v}}_i. \quad (18)$$

Case II (mixture of isotopes): With a mixture of isotopes the equations of motion for the different ion components are coupled through the collision term due to the processes represented by Eqs. (4d) and (4e). The first two collision terms in Eq. (5) have been accounted for in Case I. The evaluation of the other terms can be carried out by using the relations among the various quantities in Fig. 1. For Process (4c) terms of the type

$$\int (\mathbf{v}_i' - \mathbf{v}_i)(1-P_{ij})\lambda_{ij} d\tau_{ij} = -\xi_{ij}^a \bar{\mathbf{v}}_i \quad (19)$$

appear where ξ_{ij}^a is the average of ν_{ij}^a which is defined by

$$\nu_{ij}^a = \frac{2\pi v_{ij} n_j m_j}{m_i + m_j}\int_0^\infty (1-P_{ij})(1-\cos\theta) b db. \quad (20)$$

Process (4d) is a loss mechanism for which

$$\int \mathbf{v}_i P_{ij}\lambda_{ij} d\tau_{ij} = \xi_{ij}^l \bar{\mathbf{v}}_i, \quad (21)$$

where

$$\nu_{ij}^l = v_{ij} n_j 2\pi\int_0^\infty P_{ij} b db$$

$$= v_{ij} n_j q_c. \quad (22)$$

q_c is by the definition of P_{ij} the charge-transfer cross section. Process (4e) is a gain mechanism for which

$$\int (\mathbf{v}_i')_c P_{ji}\lambda_{ji} d\tau_{ji} = \xi_{ji}^g \bar{\mathbf{v}}_j, \quad (23)$$

where

$$\nu_{ji}^g = \frac{2\pi n_i v_{ji} m_j}{m_i + m_j}\int_0^\infty P_{ji}(1-\cos\theta) b db. \quad (24)$$

For each ion component of a mixture of isotopes the equation of motion becomes

$$\frac{\partial \bar{\mathbf{v}}_i}{\partial t} = \frac{q_i \mathbf{E}(t)}{m_i} + \frac{q_i \bar{\mathbf{v}}_i \times \mathbf{H}}{m_i c} - \xi_{ii}^c \bar{\mathbf{v}}_i - \sum_{j\neq i}(\xi_{ij}^a + \xi_{ij}^l)\bar{\mathbf{v}}_i + \sum_{j\neq i}\xi_{ji}^g (n_j^+/n_i^+)\bar{\mathbf{v}}_j. \quad (25)$$

III. SOLUTION OF THE EQUATION OF MOTION AND CALCULATION OF POWER ABSORPTION

The field directions are to be taken as

$$\mathbf{H} = H\mathbf{k}, \quad (26)$$

$$\mathbf{E}(t) = E_0 \sin\omega t\,\mathbf{i}. \quad (27)$$

The linearly polarized electric field is resolved into two counter-rotating circularly polarized components,

$$E_1(t) = \tfrac{1}{2}E_0 \sin\omega t\,\mathbf{i} + \tfrac{1}{2}E_0\cos\omega t\,\mathbf{j}, \quad (28a)$$

$$E_2(t) = \tfrac{1}{2}E_0 \sin\omega t\,\mathbf{i} - \tfrac{1}{2}E_0\cos\omega t\,\mathbf{j}. \quad (28b)$$

Only the field rotating in the same sense as the ion is of importance in determining the absorption of energy as long as $\Delta\omega/\omega_c \ll 1$ where $\Delta\omega$ is a measure of the linewidth. The power absorption from the alternating electric field by the ion component i is given by

$$A_i = \langle \mathbf{E}(t)\cdot n_i^+ q_i \bar{\mathbf{v}}_i\rangle_{Av}, \quad (29)$$

where the brackets indicate a time average. The ion velocity is transformed into a coordinate system rotating with the electric field by writing

$$\bar{v}_{xi} = u_i \sin\omega t + w_i\cos\omega t, \quad (30a)$$

$$\bar{v}_{yi} = u_i\cos\omega t - w_i \sin\omega t. \quad (30b)$$

Equation (29) then becomes

$$A_i = \tfrac{1}{2} n_i^+ q_i E_0 u_i. \quad (31)$$

The dispersion D_i is given by

$$D_i=\tfrac{1}{2}n_i^+q_iE_0w_i. \tag{32}$$

Since A_i and D_i are observed under steady-state conditions,

$$\partial u_i/\partial t=\partial w_i/\partial t=0. \tag{33}$$

Making the appropriate substitutions into Eq. (14) and setting the coefficients of $\sin\omega t$ and $\cos\omega t$ equal to zero gives for elastic collisions

$$(\omega-\omega_{ci})u_i+\sum_j\xi_{ij}^e w_i=0 \tag{34a}$$

and

$$-(\omega-\omega_{ci})w_i+\sum_j\xi_{ij}^e u_i=q_iE_0/2m_i. \tag{34b}$$

The solution of Eqs. (34) yields

$$A_i=(n_i^+q_i^2E_0^2/4m_i)\times\{\sum_j\xi_{ij}^e/[(\omega-\omega_{ci})^2+(\sum_j\xi_{ij}^e)^2]\} \tag{35a}$$

and

$$D_i=(n_i^+q_i^2E_0^2/4m_i)\times\{(\omega_{ci}-\omega)/[(\omega-\omega_{ci})^2+(\sum_j\xi_{ij}^e)^2]\}. \tag{35b}$$

Equations (35) are valid for any cyclotron resonance spectrum where the ion equations of motion for the different components are not mixed in the collision term, provided that the appropriate collision frequencies are employed. Substitution of ξ_{ii}^c for the summation over elastic collision frequencies in Eqs. (35) gives the absorption and dispersion for a single-ion isotope moving in its parent gas [where the collision term in the equation of motion is as given by Eq. (18)].

For a mixture of isotopes (Case II above) the appropriate substitutions are made in Eq. (25) which reduces to

$$(\omega-\omega_{ci})u_i+[\xi_{ii}^c+\sum_{j\neq i}(\xi_{ij}^a+\xi_{ij}^l)]w_i-\sum_{j\neq i}\xi_{ji}^g(n_j^+/n_i^+)w_j=0 \tag{36a}$$

and

$$-(\omega-\omega_{ci})w_i+[\xi_{ii}^c+\sum_{j\neq i}(\xi_{ij}^a+\xi_{ij}^l)]u_i-\sum_{j\neq i}\xi_{ji}^g(n_j^+/n_i^+)u_j=q_iE_0/2m_i. \tag{36b}$$

Equations (36) are easily solved on a computer. The ratios n_j^+/n_i^+ are determined by the system of equations describing the steady-state ion concentrations

$$dn_i^+/dt=\sum_j(-\xi_{ij}^l n_i^++\xi_{ji}^l n_j^+)=0. \tag{37}$$

At thermal equilibrium the ratios of ion densities will be determined by the corresponding isotopic ratios in the parent gas. An ion near resonance is heated, upsetting the ion density ratios from their thermal equilibrium values.

The increase of the ion velocity near resonance complicates the above calculation of the power absorption. The collision frequencies, as shown in Sec. IV, vary with velocity. It is assumed that each ion component i has a temperature T_i^* defined by the relation

$$\tfrac{1}{2}m\langle v_i^2\rangle_{Av}=\tfrac{3}{2}kT_i^*. \tag{38}$$

Substitution of $X(\mathbf{v}_i)=v_i^2$ into Eq. (5) gives (for elastic collisions, no charge transfer)

$$\frac{\partial}{\partial t}(n_i^+\langle v_i^2\rangle_{Av})=\frac{2q_in_i^+}{m_i}\mathbf{E}(t)\cdot\bar{\mathbf{v}}_i+\sum_j\int[(v_i')^2-v_i^2]\lambda_{ij}d\tau_{ij}. \tag{39}$$

It is assumed that the left-hand side of Eq. (39) vanishes under steady-state conditions. The first term on the right of Eq. (39) is related to the power absorption defined by Eq. (29) such that

$$A_i=\tfrac{1}{2}m_i\sum_j\int[v_i^2-(v_i')^2]\lambda_{ij}d\tau_{ij}. \tag{40}$$

Combining Eqs. (6) and (7) gives

$$\mathbf{v}_i=\mathbf{V}_c+[m_j/(m_i+m_j)]\mathbf{v}_{ij}. \tag{41a}$$

Similarly,

$$\mathbf{v}_i'=\mathbf{V}_c+[m_j/(m_i+m_j)]\mathbf{v}_{ij}'. \tag{41b}$$

Squaring Relations (41) and combining the results gives

$$\begin{aligned}(v_i)^2-(v_i')^2&=[2m_j/(m_i+m_j)]\mathbf{V}_c\cdot(\mathbf{v}_{ij}-\mathbf{v}_{ij}')\\&=[2m_j/(m_i+m_j)^2](m_i\mathbf{v}_i+m_j\mathbf{V}_j)\cdot(\mathbf{v}_{ij}-\mathbf{v}_{ij}').\end{aligned} \tag{42}$$

Averaging over the azimuth and omitting the terms on the right of Eq. (42) which vanish on integration over $d\mathbf{V}_j$ reduces Eq. (40) for elastic collisions to

$$A_i=\tfrac{1}{2}m_i\sum_j\int\frac{4\pi m_j}{(m_i+m_j)^2}(1-\cos\theta)\times(m_iv_i^2-m_jV_j^2)v_{ij}bdbf(\mathbf{v}_i)F(\mathbf{V}_j)d\mathbf{v}_id\mathbf{V}_j. \tag{43}$$

As was done in Eq. (13) it is necessary to factor Eq. (43) to obtain useful results. Using the definition of ξ_{ij}^e in Eq. (19) gives

$$A_i=n_i^+\sum_j[m_i\xi_{ij}^e/(m_i+m_j)](m_i\langle v_i^2\rangle_{Av}-m_j\langle V_j^2\rangle_{Av}). \tag{44}$$

Making the substitution $m_j\langle V_j^2\rangle_{Av}=3kT$, Eq. (44) can be solved for $\langle v_i^2\rangle_{Av}$ such that

$$\langle v_i^2\rangle_{Av}=\frac{(A_i/n_i^+)+3kT\sum_j[m_i\xi_{ij}^e/(m_i+m_j)]}{\sum_j[m_i^2\xi_{ij}^e/(m_i+m_j)]}. \tag{45}$$

In the limit $A_i \rightarrow 0$, Eq. (45) yields the correct limit

$$\langle v_i^2 \rangle_{Av} = 3kT/m_i.$$

The effects of charge transfer on ion temperature can be again treated according to the Cases I and II discussed in Sec. II.

Case I (*single isotope*): The inclusion of charge transfer for an ion moving in its parent gas results in the substitution of ξ_{ii}^c for ξ_{ij}^e in Eq. (45) to give

$$\langle v_i^2 \rangle_{Av} = (2A_i/n_i^+ \xi_{ii}^c m_i) + (3kT/m_i). \quad (46)$$

Case II (*mixture of isotopes*): In this case $\langle v_i^2 \rangle_{Av}$ can be obtained only as the solution of a system of linear equations. Using Eq. (5) and making the same assumptions used to derive Eq. (40) gives [using the result in Eq. (46) to evaluate the first two collision terms in Eq. (5)]

$$A_i = \tfrac{1}{2} n_i^+ \xi_{ii}^c (m_i \langle v_i^2 \rangle_{Av} - 3kT) + \tfrac{1}{2} m_i \sum_{j \neq i} \int [v_i^2 - (v_i')^2](1 - P_{ij}) \lambda_{ij} d\tau_{ij}$$

$$+ \tfrac{1}{2} m_i \sum_{j \neq i} \int v_i^2 P_{ij} \lambda_{ij} d\tau_{ij} - \tfrac{1}{2} m_i \sum_{j \neq i} \int (v_i')^2{}_c P_{ji} \lambda_{ji} d\tau_{ji}. \quad (47)$$

Evaluation of the last three terms of Eq. (47) is quite straightforward, yielding

$$\int [v_i^2 - (v_i')^2](1 - P_{ij}) \lambda_{ij} d\tau_{ij} = \frac{2\xi_{ij}^a n_i^+}{m_i + m_j} (m_i \langle v_i^2 \rangle_{Av} - 3kT), \quad (48a)$$

$$\int v_i^2 P_{ij} \lambda_{ij} d\tau_{ij} = \xi_{ij}^l n_i^+ \langle v_i^2 \rangle_{Av}, \quad (48b)$$

$$\int (v_i')^2{}_c P_{ji} \lambda_{ji} d\tau_{ji} = \xi_{ji}^l n_j^+ \frac{3kT}{m_i} + \frac{2m_j n_j^+}{m_i(m_i + m_j)} (m_j \langle v_j^2 \rangle_{Av} - 3kT)(\xi_{ji}^e - \xi_{ji}^a). \quad (48c)$$

Equation (48c) is derived in Appendix II. With these results Eq. (47) becomes

$$A_i = n_i^+ \xi_{ii}^c (\tfrac{1}{2} m_i \langle v_i^2 \rangle_{Av} - \tfrac{3}{2} kT) + 2n_i^+ (\tfrac{1}{2} m_i \langle v_i^2 \rangle_{Av} - \tfrac{3}{2} kT) \sum_{j \neq i} (\xi_{ij}^a m_i / m_i + m_j)$$

$$+ \tfrac{1}{2} n_i^+ m_i \langle v_i^2 \rangle_{Av} \sum_{j \neq i} \xi_{ij}^l - \tfrac{3}{2} kT \sum_{j \neq i} n_j^+ \xi_{ji}^l - 2 \sum_{j \neq i} \frac{m_j n_j^+}{m_i + m_j} (\tfrac{1}{2} m_j \langle v_j^2 \rangle_{Av} - \tfrac{3}{2} kT)(\xi_{ji}^e - \xi_{ji}^a). \quad (49)$$

Equation (49) represents a linear system of equations for the $\langle v_i^2 \rangle_{Av}$ which can be solved and used to obtain the ion temperatures as defined by Eq. (38). The process is an iterative one in the general case. In Eq. (49), for instance, the $\langle v_i^2 \rangle_{Av}$ depend on the power absorptions and collision frequencies. If an initial guess is made for the collision frequencies, the power absorptions can be calculated from a solution of Eqs. (36). Then with Eqs. (49) the ion temperatures can be obtained and employed to calculate a new set of collision frequencies. The procedure usually converges fairly rapidly because of the monotonic variation of the collision frequencies with temperature (Sec. IV).

Once the ion temperatures are obtained the averaged collision frequencies can be calculated from their definition as in Eq. (13),

$$\xi_{ij} = (n_j n_i^+)^{-1} \int \nu_{ij} f(\mathbf{v}_i) F(\mathbf{V}_j) d\mathbf{v}_i d\mathbf{V}_j, \quad (50)$$

where ν_{ij} is any one of the several collision frequencies. The ion distribution function for component i is taken as Maxwellian about the ion temperature T_i^*. The averaging procedure is simplified by noting that ν_{ij} depends on the magnitude of the relative velocity vector and not on v_i or V_j separately. Because of this it is possible to reduce Eq. (50) to

$$\xi_{ij} = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{\mu_{ij}^*}{kT}\right)^{3/2} \int_0^\infty \nu_{ij} \exp\left(\frac{-\mu_{ij}^* v_{ij}^2}{2kT}\right) v_{ij}^2 dv_{ij}, \quad (51)$$

where μ_{ij}^* is defined by

$$\mu_{ij}^* = T m_i m_j / (T m_i + T_i^* m_j). \quad (52)$$

IV. ION-MOLECULE INTERACTIONS AND EVALUATION OF THE COLLISION FREQUENCIES

The Lennard-Jones potential is a reasonable approximation to the interaction between neutral molecules for the study of transport properties.[10] The addition of an attractive polarization potential to the Lennard-Jones potential has been used as a model for ion-molecule interactions.[11] This potential is given by

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] - (\alpha e^2/2r^4), \quad (53)$$

where the parameters ϵ and σ which fit the Lennard-

[10] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 22.

[11] H. K. Shin, J. Chem. Phys. **42**, 1739 (1965).

Jones potential to the system being considered are tabulated in Ref. 10. α is the angle-averaged polarizability of the neutral species involved in the collision. Equation (53) is to be taken only as representative of the gross features of the interaction and neglects any exchange forces which might in some cases be important. There are two primary features to the interaction. The first of these is that the long-range part of the interaction is dominated by the r^{-4} polarization attraction. The second is that the potential shows a very sharp repulsive wall which makes the hard-sphere model fairly reasonable for close or "hard" collisions.

A. Elastic Collisions

Wannier[12,13] has shown that the orbits of particles under the influence of long-range attractive r^{-4} potential can be divided into two classes. At large impact parameters the orbit is open with only a slight defection (small θ). At a critical impact parameter b_{ij}^0 given by

$$b_{ij}^0=(4e^2\alpha/\mu_{ij}v_{ij}^2)^{1/4}, \tag{54}$$

where $\mu_{ij}=m_im_j/(m_i+m_j)$, the open orbits become inward spirals. b_{ij}^0 is known commonly as the impact parameter for orbiting collisions. In the evaluation of integrals of the type $\int(1-\cos\theta)bdb$ it has been shown that b_{ij}^0 serves conveniently to separate small angle deflections from large angle deflections such that to a good approximation[12]

$$2\pi\int_0^\infty(1-\cos\theta)bdb\approx\pi(b_{ij}^0)^2. \tag{55}$$

The behavior at the repulsive wall is represented by a classical hard-sphere model. The relation between θ and b is given exactly in this case by

$$b=b_{ij}^h\cos(\tfrac{1}{2}\theta), \tag{56}$$

where

$$b_{ij}^h=b_i^h+b_j^h \tag{57}$$

and b_i^h and b_j^h are, respectively, the ionic and neutral hard-sphere radii of ion i and neutral j. The hard-sphere cross section replaces the orbiting cross section when the latter is less than the former:

$$\begin{aligned}q_D&=2\pi\left[\int_0^{b_{ij}^h}(1-\cos\theta)bdb+h(b_{ij}^0-b_{ij}^h)\int_{b_{ij}^h}^{b_{ij}^0}(1-\cos\theta)bdb\right]\\&=\pi(b_{ij}^h)^2+\pi h(b_{ij}^0-b_{ij}^h)[(b_{ij}^0)^2-(b_{ij}^h)^2],\end{aligned} \tag{58}$$

where

$$\begin{aligned}h(x)&=1 \quad \text{for} \quad x>0\\&=0 \quad \text{for} \quad x<0.\end{aligned}$$

It is not meaningful to speak of an orbiting cross section when b_{ij}^0 is less than b_{ij}^h. Using Eq. (58) for q_D permits the evaluation of ν_{ij}^e as defined by Eq. (11).

B. Charge Transfer

Ions in their parent gases can undergo symmetric resonant charge transfer, the process being represented as

$$A+A^+\rightarrow A^++A. \tag{59}$$

This process is important because the charge-transfer cross sections for monatomic and most diatomic ions in their present gases are large compared to the hard-sphere cross sections.[14,15] Diatomic ions have small charge-transfer cross sections whenever there is considerable disparity between the equilibrium internuclear distances of the ion and the neutral molecule. This is reflected in the vibrational overlap integral between the incident and scattered states.[16] Charge-transfer cross section at low energies are usually calculated employing the method of perturbed stationary states.[14,16,17] Firsov's[17] calculations have found a wide applicability, fitting well the experimental cross section of monatomic ions in their parent gases. It is found[16,17] that for a given velocity the charge-transfer probability varies rapidly between zero and unity for impact parameters up to b^c, after which the probability rapidly decreases. The charge-transfer cross section is then given by $q_c\approx\frac{1}{2}\pi(b^c)^2$. Firsov's[17] results give b^c as the solution to

$$\begin{aligned}\beta b^c-(2\gamma-\tfrac{1}{2})\ln(\beta b^c)-[(\gamma-\tfrac{1}{8})/\beta b^c]\\=\ln[(2\pi^3)^{1/2}\beta\hbar/(2\gamma)!m_ev],\end{aligned} \tag{60}$$

where $\gamma=(m_ee^4/2\hbar^2I)^{1/2}$, $\beta=(2m_eI/\hbar^2)^{1/2}$, I is the first ionization potential, and v is the relative velocity between the ion and molecule. Equation (60) does not account for deflections of the particle, as b_{ii}^c is usually larger than b_{ii}^0. At low velocities, however, b_{ii}^0 exceeds b_{ii}^c as calculated from Eq. (60). In this region b_{ii}^c can be replaced by b_{ii}^0 since it is reasonable to assume that in the case of an orbiting collision the probability of charge transfer is $\frac{1}{2}$. In the high velocity region b_{ii}^c is taken to be b_{ii}^h for b_{ii}^c less than b_{ii}^h. This assumption

[12] G. H. Wannier, Bell System Tech. J. **32**, 70 (1953), Sec. IIIB.
[13] E. Vogt and G. H. Wannier, Phys. Rev. **95**, 1190 (1954).
[14] J. B. Hasted, in *Atomic and Molecular Processes*, D. R. Bates, Ed. (Academic Press Inc., New York, 1962), p. 696.
[15] E. W. McDaniel, *Collision Phenomena in Ionized Gases* (John Wiley & Sons, Inc., New York, 1964), p. 240.
[16] E. F. Gurnee and J. L. Magee, J. Chem. Phys. **26**, 1237 (1957).
[17] O. B. Firsov, Zh. Eksperim. i Teor. Fiz. **21**, 1001 (1951) (reviewed in Ref. 14).

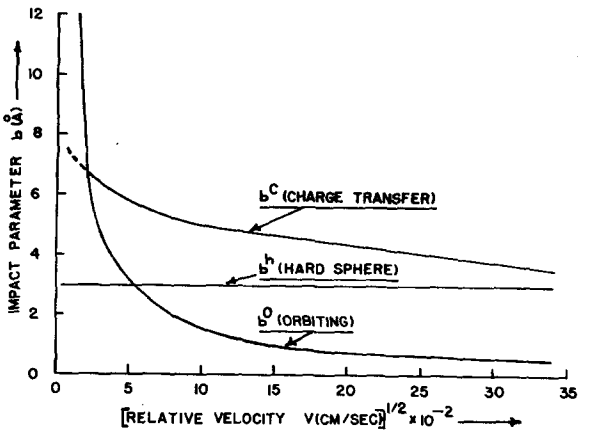

FIG. 2. Variation of impact parameters for orbiting collisions, hard-sphere collisions, and charge transfer with velocity for argon ions in argon. The dashed line shows the continuation of Firsov's calculation.

is inaccurate at very high velocities since the time of interaction of the two particles in a collision decreases and the exchange interaction as employed in the perturbed stationary state framework is accordingly reduced. Figure 2 shows for comparison b_{ii}^0, b_{ii}^c, and b_{ii}^h for argon ions in argon. b_{ii}^h is determined by the point at which $V(r)=0$.

For diatomic ions b_{ii}^c can be calculated as in Ref. 16 with proper allowance being made for vibrational overlap and rotational averaging. However, the agreement between theoretical and experimental cross sections in this case is not very satisfactory.[16]

The remainder of the various collision frequencies appearing in the previous section can now be evaluated. Charge transfer has been included in Eq. (17) for ν_{ii}^c (and the other collision frequencies where charge transfer is considered) so as not to affect the relations between b and $\cos\theta$ which were developed above for elastic collisions. Thus, θ remains as defined in Fig. 1 regardless of whether or not charge transfer occurs. P_{ii} can be taken as $\frac{1}{2}$ up to b_{ii}^c and zero beyond b_{ii}^c. Equation (17) thus becomes

$$\nu_{ii}^c = n_i v_{ii} \pi \left(\int_0^\infty (1-\cos\theta) b db + 2 \int_0^\infty b db P_{ii} \cos\theta \right)$$
$$= \tfrac{1}{2} n_i v_{ii} \pi (b_{ii}^c)^2 = n_i v_{ii} q_c. \quad (61)$$

Comparing Eqs. (22) and (61) yields $\nu_{ij}^l = \nu_{ij}^c$. Evaluating the integral in Eq. (20) gives

$$\nu_{ij}^a = \frac{2\pi v_{ij} n_j m_j}{m_i+m_j} \int_0^\infty (1-P_{ij})(1-\cos\theta) b db = \tfrac{1}{2}\nu_{ij}^e. \quad (62)$$

Finally, ν_{ji}^a in Eq. (25) becomes

$$\nu_{ji}^a = 2\pi n_i v_{ji} \frac{m_j}{m_i+m_j} \int_0^\infty P_{ji}^c (1-\cos\theta) b db$$
$$= \frac{\pi n_i v_{ji} m_j}{m_i+m_j} \int_0^{b_{ii}^c} (1-\cos\theta) b db$$
$$= m_j \nu_{ji}^e / 2m_i. \quad (63)$$

V. APPLICATIONS

Using the formalism developed above it is possible to calculate cyclotron resonance spectra in detail, including the effects of pressure and electric-field broadening. For the rare gases the various collision frequencies in the equations of motion for the ion current and the ion temperature reduce to functions of the two collision frequencies, ξ^c and ξ^e. These collision frequencies depend on cross sections which can be evaluated in terms of the impact parameters for orbiting collisions, hard-sphere interactions, and charge transfer. Using the impact parameters shown in Fig. 2 for argon, ξ^c and ξ^e are evaluated and shown in Fig. 3. The collision frequencies are given as functions of the ion temperature T^*, with the temperature of the neutral scattering gas being held at 323°K. The collision frequencies are normalized to a scattering gas density of 1 molecule/cm^3.

ξ^c and ξ^e for argon are typical of the rest of the rare gases in their variation with temperature. ξ^c shows a monotonic increase, approximately proportional to the square root of the ion temperature. The elastic collision frequency, ξ^e, is independent of ion temperature up to 20 000°K because of the dominance of the orbiting interaction at low relative velocities. Above 20 000°K hard-sphere collisions dominate and ξ^e rises in direct proportion to the square root of ion temperature. For the rare gases the velocity averaging of the collision frequencies ν, to obtain the corresponding ξ results in only a 2% to 3% difference from what is obtained by using the average ion–molecule relative velocity determined simply from the ion and neutral temperatures.

The collision frequencies obtained as a function of the ion temperatures can be employed in conjunction with Eqs. (36) and (49) to calculate the power absorption. The three spectra shown in Fig. 4 are calculated using the collision frequencies given for argon in Fig. 3. The absorption curves in Fig. 4 are normalized by dividing by the square of the electric-field strengths in order to display directly the effect which the variation of the collision frequency with electric-field strength has on the spectra. The pressure used in the calculation

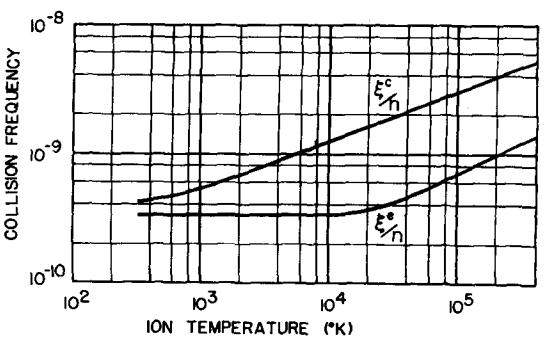

FIG. 3. Collision frequencies calculated for argon ions in neutral argon with $T=323$°K. ξ^c and ξ^e are normalized to n, the scattering gas density.

is 6.8×10^{-4} torr. The magnetic field is not specified since the absorption depends only on the difference $|\omega-\omega_c|$. With an electric field of 0.00085 V/cm (practical volts are employed) the ions are not heated beyond the temperature of the neutrals, again assumed at 323°K. At 0.085 V/cm the resonance is slightly broadened. With $E_0=0.85$ V/cm, the normalized absorption is considerably broadened by the heating of the ions at resonance. The normalized absorption spectra become identical at large values of $|\omega-\omega_c|$ for which the ion temperature approaches that of the neutral gas.

It is of interest to apply the above formalism to a mixture of ^{3}He and ^{4}He. Figure 5 shows the spectrum calculated for an equimolar mixture of ^{3}He and ^{4}He at a total pressure of 0.01 torr and an observing electric-field level of 0.10 V/cm. The spectrum is calculated as a function of magnetic field with the oscillator fixed at 1.538 Mc/sec. At this frequency the $^3He^+$ and $^4He^+$ resonances occur at 3.0 and 4.0 kG, respectively. The absorption varies inversely with particle mass giving rise to the apparent relative intensities in Fig. 5. At resonance the ion temperature varies as $(E/P)^2$ if the collision frequency is independent of velocity. At the relatively high pressure of 0.01 torr the ions are not appreciably heated by the electric field, with the $^3He^+$ rising only to 425°K at its resonance. At 3.0 kG the $^4He^+$ temperature rises slightly due to charge-transfer collisions as indicated by Eq. (53) in which a deflection of the particles also occurs. The transfer term in the equation of motion for the ion temperature responsible for this heating of the $^4He^+$ is that given by Eq. (48c). $^3He^+$ is likewise slightly heated when the $^4He^+$ undergoes resonance at 4.0 kG. The ratio of ion densities as calculated from Eq. (37) is shown by the upper trace in Fig. 5. The ratio of $^3He^+/^4He^+$ decreases at 3.0 kG when the $^3He^+$ is heated to a temperature above that of the $^4He^+$, forcing the following reaction to the right:

$$^3He^+ + {}^4He \rightleftarrows {}^3He + {}^4He^+. \qquad (64)$$

At 4.0 kG the reaction is driven to the left when the $^4He^+$ is heated. This "pumping" of ions is not directly

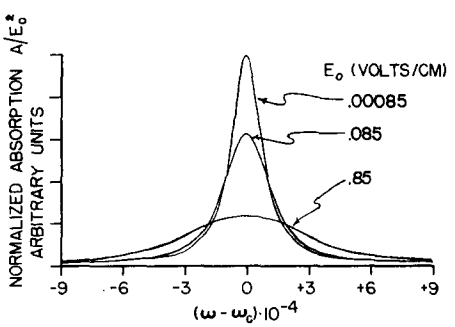

FIG. 4. Normalized cyclotron resonance power absorption calculated for argon ions in neutral argon for $T=323$°K and $p=6.8\times10^{-4}$ torr.

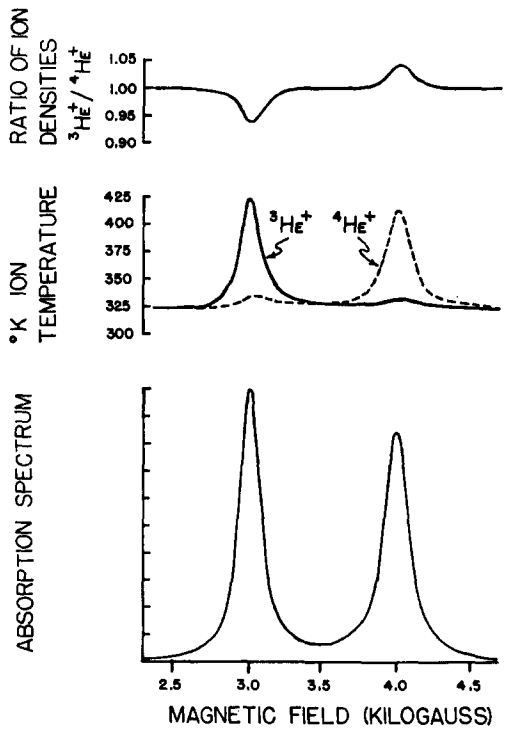

FIG. 5. Field-sweep cyclotron resonance spectrum, ion temperatures, and relative ion densities calculated for an equimolar mixture of ^{3}He and ^{4}He where $P=0.01$ torr, $E_0=0.1$ V/cm, and $\omega=1.538$ Mc/sec.

evident in the spectrum shown in Fig. 5. This is because both absorptions are decreased by about the same amount.

The effect of the ion pumping is much more evident in the calculated spectrum of two isotopes of neon shown in Fig. 6. The conditions assumed in Fig. 6 are ^{20}Ne pressure 3.0×10^{-4} torr, ^{22}Ne pressure 3.0×10^{-5} torr, neutral gas temperature 323°K, observing oscillator frequency 768.0 kc/sec, and at an electric field of 0.50 V/cm. The natural isotopic abundances of ^{20}Ne and ^{22}Ne are in a ratio of 10.30:1. At the relatively high level of the electric field used in Fig. 6 the peak heights of $^{20}Ne^+$ and $^{22}Ne^+$ are in a ratio much greater than 10:1. This is due to charge exchange of the $^{22}Ne^+$ with ^{20}Ne represented by

$$^{22}Ne^+ + {}^{20}Ne \rightleftarrows {}^{22}Ne + {}^{20}Ne^+. \qquad (65)$$

Because of the relative concentrations of the neutrals involved the pumping is much more effective from left to right in Eq. (65). In Fig. 6 it is also evident that the $^{20}Ne^+$ heats the $^{22}Ne^+$ to 5000°K at 10.0 kG while the $^{22}Ne^+$ is relatively ineffective in heating the $^{20}Ne^+$ at 11.0 kG. Because of the relative numbers of $^{20}Ne^+$ and $^{22}Ne^+$ ions the heat capacity of the $^{20}Ne^+$ is much larger than that of the $^{22}Ne^+$. The ratio of ion densities shown in Fig. 6 illustrates the extent of the ion pumping, and indicates that the $^{22}Ne^+$ ion density (normally ~10% of the total ion density) can be

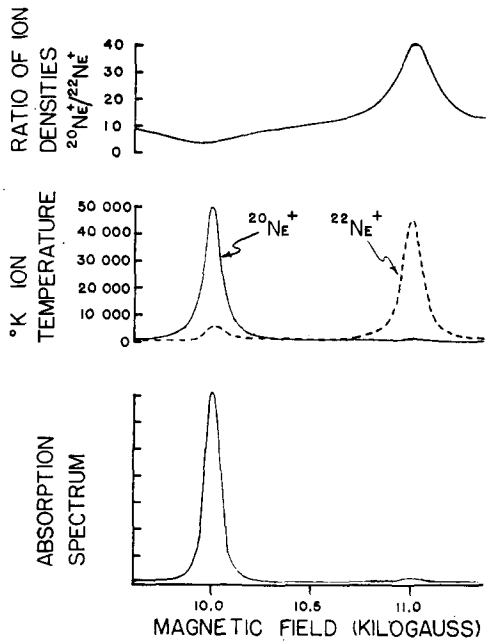

FIG. 6. Field-sweep cyclotron resonance spectrum, ion temperatures, and relative ion densities calculated for a mixture of ^{20}Ne and ^{22}Ne where $P(^{20}Ne)=3.0\times10^{-4}$ torr, $P(^{22}Ne)=3.0\times10^{-5}$ torr, $T=323°K$, $\omega=768.0$ kc/sec, and $E_0=0.5$ V/cm.

enhanced to nearly 25% with the application of a moderate electric field at the $^{20}Ne^+$ cyclotron resonance frequency.

The upper trace of Fig. 6 appears also in Fig. 7 along with several other calculations showing the variation of the ratio of ion densities with electric field. At 0.01 V/cm the ratio of ion densities changes only slightly, and the peak heights in the calculated absorption spectrum are in the same ratio as the neutral parent species.

VI. DISCUSSION

The formalism described for the calculation of collision-broadened ion cyclotron resonance spectra can be extended to include processes such as inelastic collisions and ion–molecule reactions. Chemical reaction, like charge transfer, couples the equations of motion for different ion components.[18] The above formalism is also readily extended to describe the various possible multiple cyclotron resonance experiments.[18,19]

The procedure described in this paper appears to form a useful basis for the calculation of ion cyclotron resonance line shapes under a variety of conditions, and can be refined by using more elaborate methods for the evaluation of the collision integrals. The diffusion cross section is important in almost all ion transport phenomena. Ion mobilities are in particular inversely proportional to the diffusion cross section.[20] Because of this the ion cyclotron resonance linewidths are also inversely related to the ion mobilities, and the literature relevant to the calculation of ion mobilities can be applied to the evaluation of the cyclotron resonance collision frequencies.[20]

The sample calculations suggest that ion cyclotron resonance will have considerable practical interest as a technique for the direct study of ion–molecule interactions.

ACKNOWLEDGMENTS

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APPENDIX I: EXTENSION OF BOLTZMANN TRANSPORT EQUATION FOR MOLECULAR PROPERTIES TO INCLUDE CHARGE TRANSFER

Inclusion of charge-transfer effects in the Boltzmann equation has been treated for the pure charge-transfer case by Kagen and Perel.[21] In Ref. 21 a model is assumed for which charge exchange occurs on every collision. This assumption is avoided by letting P_{ij} be the probability of charge transfer in a collision between ion i and neutral j. The collision term in the Boltzmann equation can be written

$$[\partial f(\mathbf{v}_i)/\partial t]_{\text{coll}} = \sum_j (E_{ij}^{(+)} - E_{ij}^{(-)}) + \sum_j (C_{ji}^{(+)} - C_{ij}^{(-)}), \quad \text{(A1)}$$

where the left-hand side represents the time rate of

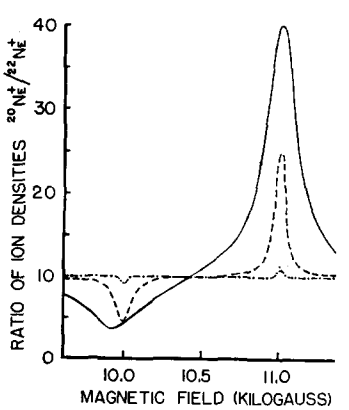

FIG. 7. $^{20}Ne^+/^{22}Ne^+$ ratio of ion densities calculated for various values of E_0 with $P(^{20}Ne)=3.0\times10^{-4}$ torr, $P(^{22}Ne)=3.0\times10^{-5}$ torr, $T=323°K$, and $\omega=768.0$ kc/sec. $-\cdot-$, $E_0=0.01$ V/cm; $----$, $E_0=0.10$ V/cm; ——, $E_0=0.50$ V/cm.

[18] L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, J. Chem. Phys. **45**, 1062 (1966).

[19] J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler (to be published).

[20] See, for instance, A. Dalgarno, in *Atomic and Molecular Processes*, D. R. Bates, Ed. (Academic Press Inc., New York, 1962), Chap. 16 and references contained therein.

[21] M. Kagen and V. I. Perel, Soviet Phys.—JETP **8**, 87 (1958) [Zh. Eksperim. i Teor. Fiz. **34**, 126 (1958)].

change of the distribution function due to collisions. The total increase in the number of particles with velocities within $d\mathbf{v}_i$ of $\mathbf{v}_i$ during an element of time dt is given by

$$[\partial f(\mathbf{v}_i)/\partial t]_{\text{coll}}\, d\mathbf{v}_i dt. \tag{A2}$$

The individual contributions to (A2) are given on the right side of (A1). $E_{ij}^{(+)}$ and $E_{ij}^{(-)}$ represent respectively the gain and loss of particles due to elastic collisions in which no charge transfer occurs. $C_{ij}^{(-)}$ represents the loss of ions i due to charge transfer to neutrals j. $C_{ji}^{(+)}$ represents the gain of ions i resulting from charge transfer from ions j to neutrals i. The term with $j=i$ appears in both sums. An implicit assumption is that the total number of ions [to which $f(\mathbf{v}_i)$ is normalized] does not change with time.

Following the treatment in Ref. 10 it is assumed that the interaction potential for elastic scattering is effective over a distance A. In Fig. 8 it is assumed that i is fixed and neutral j approaches with an impact parameter between b and $b+db$, scattering azimuth between ϵ and $\epsilon+d\epsilon$, and velocity between $\mathbf{V}_j$ and $\mathbf{V}_j+d\mathbf{V}_j$. All such particles j in the cylindrical shell shown in Fig. 8 interact with i in the time element dt resulting in i being removed from within $d\mathbf{v}_i$ of $\mathbf{v}_i$ in velocity space. The total number of collisions of neutrals j with a single i in time dt is given by

$$dt\iiint_A (1-P_{ij})F(\mathbf{V}_j)v_{ij}bdbd\epsilon d\mathbf{V}_j. \tag{A3}$$

The probable number of ions of type i with velocity in the range $d\mathbf{v}_i$ about $\mathbf{v}_i$ is $f(\mathbf{v}_i)d\mathbf{v}_i$. Thus

$$E_{ij}^{(-)}d\mathbf{v}_i dt = d\mathbf{v}_i dt\iiint_A (1-P_{ij})F(\mathbf{V}_j)f(\mathbf{v}_i)v_{ij}bdbd\epsilon d\mathbf{V}_j, \tag{A4}$$

such that

$$E_{ij}^{(-)} = \iiint_A (1-P_{ij})F(\mathbf{V}_j)f(\mathbf{v}_i)v_{ij}bdbd\epsilon d\mathbf{V}_j. \tag{A5}$$

Since different forces are responsible for charge transfer, the effective interaction distance must be changed to A'. Charge transfer results in a loss of particles in a given velocity element. Following a line of argument similar to that above gives $C_{ij}^{(-)}$ as

$$C_{ij}^{(-)} = \iiint_{A'} P_{ij}F(\mathbf{V}_j)f(\mathbf{v}_i)v_{ij}bdbd\epsilon d\mathbf{V}_j. \tag{A6}$$

If it were not for the subtle difference between A and A' it would appear that $E_{ij}^{(-)}$ and $C_{ij}^{(-)}$ could be added directly together with considerable simplification.

To obtain the supply terms we need to consider collisions which are the reverse of the loss terms. Following the collision we have $v_{ij}'=v_{ij}$ and $b'=b$. Furthermore, for a given b, g_{ij}, and ϵ, the dynamical equations relating $\mathbf{v}_i$ and $\mathbf{V}_j$ to $\mathbf{v}_i'$ and $\mathbf{V}_j'$ require that if time were reversed then $\mathbf{v}_i'$ and $\mathbf{V}_j'$ would scatter back to $\mathbf{v}_i$ and $\mathbf{V}_j$ in velocity space. To obtain the number of ions scattered back to within $d\mathbf{v}_i$ of $\mathbf{v}_i$ in time element dt it is necessary to integrate over all collisions which are the reverse of those leading to particle loss. For elastic collisions this is

$$E_{ij}^{(+)}d\mathbf{v}_i dt = d\mathbf{v}_i' dt \times\iiint_A f(\mathbf{v}_i')F(\mathbf{V}_j')(1-P_{ij})v_{ij}bdbd\epsilon d\mathbf{V}_j'. \tag{A7}$$

Chapman and Cowling[6] have shown that

$$d\mathbf{v}_i d\mathbf{V}_j = d\mathbf{v}_i' d\mathbf{V}_j', \tag{A8}$$

even in the presence of electric and magnetic fields, the Jacobian of the transformation being unity. Substituting (A8) into (A7) gives

$$E_{ij}^{(+)} = \iiint_A f(\mathbf{v}_i')F(\mathbf{V}_j')(1-P_{ij})v_{ij}bdbd\epsilon d\mathbf{V}_j. \tag{A9}$$

The number of collisions of ions j with neutrals i in time element dt which result in a charge exchange and the formation of an ion i with velocity within $d\mathbf{v}_i$ of $\mathbf{v}_i$ is given by

$$C_{ji}^{+}d\mathbf{v}_i dt = d\mathbf{V}_i' dt\iiint_{A'} P_{ji}'f(\mathbf{v}_j')F(\mathbf{V}_i')v_{ji}'bdbd\epsilon d\mathbf{v}_j'. \tag{A10}$$

$P_{ji}'=P_{ji}$ since P_{ji} is a function only of b and v_{ji}, both of which are unchanged by the collision. For collisions of this type it is quite straightforward to show that

$$d\mathbf{V}_i' d\mathbf{v}_j' = d\mathbf{v}_i d\mathbf{V}_j. \tag{A11}$$

Using (A11) in (A10) gives

$$C_{ji}^{(+)} = \iiint_{A'} P_{ji}F(\mathbf{V}_i')f(\mathbf{v}_j')v_{ji}bdbd\epsilon d\mathbf{V}_j. \tag{A12}$$

To obtain the collision term employed in the Boltzmann equation of change for a molecular property, multiply (A1) by $X(\mathbf{v}_i)d\mathbf{v}_i$ and integrate over $d\mathbf{v}_i$. Doing this

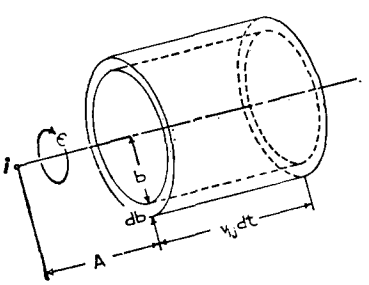

FIG. 8. Scattering of a fixed ion i by neutrals of Type j. The axis of the cylinder is collinear with V_j.

with the elastic supply term given by Eq. (A9) yields

$$\int E_{ij}^{(+)}X(\mathbf{v}_i)\,d\mathbf{v}_i=\iiiint_{A'} X(\mathbf{v}_i)F(\mathbf{V}_j')f(\mathbf{v}_i')\,(1-P_{ij})\,v_{ij}bdbd\epsilon d\mathbf{V}_j d\mathbf{v}_i. \tag{A13}$$

On the right side of (A13) the primed and unprimed velocities can be interchanged because of the reversibility of elastic collision which with relation (A9) leads to

$$\int E_{ij}^{(+)}X(\mathbf{v}_i)\,d\mathbf{v}_i=\int_{A'} X(\mathbf{v}_i')\,(1-P_{ij})\lambda_{ij}d\tau_{ij}, \tag{A14}$$

where

$$\lambda_{ij}=f(\mathbf{v}_i)F(\mathbf{V}_j)$$

$$d\tau_{ij}=v_{ij}bdbd\epsilon d\mathbf{v}_i d\mathbf{V}_j.$$

and

The charge-transfer supply term is treated similarly, starting with

$$\int C_{ji}^{(+)}X(\mathbf{v}_i)\,d\mathbf{v}_i=\iiiint_{A'} X(\mathbf{v}_i)P_{ji}F(\mathbf{V}_i')f(\mathbf{v}_j')v_{ji}bdbd\epsilon d\mathbf{V}_j d\mathbf{v}_i. \tag{A15}$$

Again because of the relation between the primed and unprimed variables we can use Eq. (A11) and change the variables of integration coordinate to obtain

$$\int C_{ji}^{(+)}X(\mathbf{v}_i)\,d\mathbf{v}_i=\int_{A'} X_c(\mathbf{v}_i')P_{ji}\lambda_{ji}d\tau_{ji}, \tag{A16}$$

where the subscript c has been inserted as a reminder that $\mathbf{v}_i'$ results from charge exchange of an ion j with a neutral i. The total time rate of change of $X(\mathbf{v}_i)$ is then given by

$$\int\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}X(\mathbf{v}_i)\,d\mathbf{v}_i\equiv\left[\frac{\partial}{\partial t}\langle X(\mathbf{v}_i)\rangle_{\text{Av}}\right]_{\text{coll}}$$

$$=\sum_j\int_A[X(\mathbf{v}_i')-X(\mathbf{v}_i)](1-P_{ij})\lambda_{ij}d\tau_{ij}+\sum_j\int_{A'}X_c(\mathbf{v}_i')P_{ji}\lambda_{ji}d\tau_{ji}-\sum_j\int_{A'}X(\mathbf{v}_i)P_{ij}\lambda_{ij}d\tau_{ij}. \tag{A17}$$

APPENDIX II: EVALUATION OF THE CHARGE-TRANSFER SUPPLY TERM IN THE ION TEMPERATURE EQUATION

A considerable amount of manipulation is required to obtain the last term in the equation for the temperature of a mixture. An ion j collides with neutral i and charge exchange occurs, resulting in $\mathbf{v}_j$ and $\mathbf{V}_i$ being scattered, respectively, to $\mathbf{V}_j'$ and $\mathbf{v}_i'$ in velocity space. The following relations follow directly:

$$\mathbf{V}_i=\mathbf{V}_c-[m_j/(m_i+m_j)]\mathbf{v}_{ji}, \tag{A18}$$

$$\mathbf{v}_i'=\mathbf{V}_c+[m_j/(m_i+m_j)]\mathbf{v}_{ij}'. \tag{A19}$$

Squaring Eqs. (A18) and (A19) and combining the results gives

$$V_i^2-(v_i')^2=-[2m_j/(m_i+m_j)]\mathbf{V}_c\cdot(\mathbf{v}_{ji}+\mathbf{v}_{ij}')$$

$$=-[2m_j/(m_i+m_j)^2](m_i\mathbf{V}_i+m_j\mathbf{v}_j)\cdot(\mathbf{v}_{ji}-\mathbf{v}_{ij}'). \tag{A20}$$

Then perform the following average, integrating over the azimuth:

$$\iiiint[V_i^2-(v_i')^2]P_{ji}v_{ji}f(\mathbf{v}_j)F(\mathbf{V}_i)\,bdbd\epsilon d\mathbf{v}_j d\mathbf{V}_i$$

$$=\frac{2m_j}{(m_i+m_j)^2}\,2\pi\iiint(m_iV_i^2-m_jv_j^2)\,(1-\cos\theta)\,P_jv_{ji}f(\mathbf{v}_j)F(\mathbf{V}_i)\,bdbd\mathbf{v}_j d\mathbf{V}_i. \tag{A21}$$

The result can be factored and rearranged to give

$$\int (v_i')^2 P_{ji}\lambda_{ji}d\tau_{ji}=n_j^+\xi_{ji}^l\frac{3kT}{m_i}+\frac{2m_jn_j^+}{m_i(m_i+m_j)}(m_j\langle v_j^2\rangle_{Av}-3kT)(\xi_{ji}^e-\xi_{ji}^a). \quad \text{(A22)}$$

The first term on the right of Eq. (A22) represents the gain of thermal ions to Ion Component i. The second term depends on the part of the interaction which results in deflections of the particles in velocity space, and accounts for the transfer of energy (in excess of thermal energy) of ions j to ions i in hard collisions which are accompanied by charge transfer.

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Glass Transition in *o*-Terphenyl

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Volumetric and thermal measurements on its undercooled liquid indicate that *o*-terphenyl undergoes a glass transition in the vicinity of −30°C. This glass temperature is about 60°C higher than that predicted by correlations applicable to simple molecular glass formers. The viscosity of the undercooled liquid was measured over the temperature range 20° to −16°C. These data and the higher-temperature data of other investigators are described approximately (between 250° and −16°C) by the equation

$$\eta=4.65\times10^{-4}\exp[689/(T-231)]\ \text{P}.$$

The apparent activation energy for viscous flow increases from about ¼ of the heat of vaporization ΔH_v at the highest part to about 5 ΔH_v at the lowest part of the temperature range. The rates of volume relaxation in the vicinity of the glass transition temperature were measured. Each relaxation isotherm could be described with a single time constant over volume changes ranging up to 0.2%. In a cylindrical dilatometer, with a large length-to-diameter ratio, the relaxation rates apparently were limited by a flow process reflecting the adhesion of terphenyl to the dilatometer walls. Approximate values of the shear viscosity were inferred from a model for this process. Apparently, the homogeneous nucleation frequency of crystals in amorphous *o*-terphenyl does not reach a measurable level. The undercooling dependence of the rate of advance of the crystallization front was measured.

I. INTRODUCTION

A CONSIDERABLE number of simple molecular compounds which are bound in the condensed state only by van der Waals forces can be undercooled readily to the glass state. Such compounds consist of molecules which are asymmetric in structure. The glass-transition characteristics of these "unassociated" systems are especially interesting from a theoretical viewpoint but are difficult to obtain experimentally because of the relatively low glass transition temperatures of most of these compounds. However, the glass-transition temperature of *o*-terphenyl is abnormally high, being of the order of −30°C. Therefore, we have investigated its volumetric and thermal behavior into the glass transition range and its viscometric behavior to −16°C. Also, we report some observations of its crystallization behavior.

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II. EXPERIMENTAL TECHNIQUES

The *o*-terphenyl used here was purchased as a stock item from Eastman Chemical Company, Rochester, New York. Two grades of *o*-terphenyl are available which are listed as "technical grade" and "highest purity", respectively. The data presented in the following sections were taken from samples of technical-grade *o*-terphenyl which had been recrystallized from methyl alcohol. This preparation gave a yield of slightly higher purity than the commercially available "highest purity," as evaluated by a melting-point determination. The resulting melting-point spread for the samples used was approximately 2°C. Samples used for volumetric and viscometric studies were melted and recrystallized several times under vacuum in order to remove traces of the methanol solvent.

The constant temperature bath used for the volumetric and viscometric studies employed a cooling jet of CO_2 gas controlled by a bimetallic thermoregulator.